



FINAL REPORT

ENVIRONMENTAL FORENSIC INVESTIGATION AT THE ASHLAND LAKEFRONT SITE IN ASHLAND, WISCONSIN

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prepared for

Northern States Power Company-WI	URS
1414 West Hamilton Avenue	10200 Innovation Drive, Suite 500
Eau Claire, WI 54701	Milwaukee, Wisconsin 53226

prepared by

**Stephen Emsbo-Mattingly, M.S.
NewFields Environmental Forensics Practice, LLC
100 Ledgewood Place, Suite 302
Rockland, Massachusetts 02370
Phone: (781) 681-5040 Fax: (781) 681-5048**

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Executive Summary

This report presents a detailed compositional description of samples collected around the Ashland Lakefront Site in Ashland, WI (Site). It identifies the nature of tar, petroleum, and wood preservatives in samples from the former Coal Tar Dump, Solid Waste Disposal Area, Wastewater Treatment Plant, and Buried Pipes with direct comparisons to Site sediment and Reference Area sediment sampling locations.

Based on advanced chemical analysis, the results of this investigation yielded the following conclusions.

- Samples from the Coal Tar Dump Area contained tar of similar composition. The signature of this tar compared well with selected NAPL samples collected by WDNR in 2001 from pipes located up gradient of the Seep Area.
- The Solid Waste Disposal Area contained tar and petroleum from a range of sources. Some of the samples resembled residues from the Coal Tar Dump Area, while other sources could not be identified.
- Many groundwater samples collected throughout Kreher Park contained diesel range petroleum that helped dissolve weathered tar with which it commingled.
- The Wastewater Treatment Plant samples contained pyrogenic PAHs most similar to tar residues from both the Solid Waste and Coal Tar Dump areas. Contributions of petrogenic PAHs from diesel and heavy range petroleums were also observed.
- The PAH concentration in many Site sediments was within or slightly above the range of Reference Area sediments. The PAH pattern in some Site sediments resembled a mixture of the regional background and tar residues evident throughout Kreher Park. These samples also contained modern organics associated with degraded vegetation; e.g., wood debris.
- Evidence in favor of the historical preservation of wood at Kreher Park was strong. It included the concentrations and compositional associations of non-MGP derived wood preserving agents like pentachlorophenol (PCP), phenols, diesel range petroleum distillates, and creosote.

These data established that subsurface samples at Kreher Park contained hydrocarbon mixtures derived from tar and petroleum that were released as part of the historical development of the Ashland shoreline. The Solid Waste Area clearly received a wide range of PAH containing materials. While some of the tar samples resembled tar from the Coal Tar Dump, the origin of many samples was unknown. The Coal Tar Dump contained tar that originated at least in part from up gradient pipes. This tar was likely amended with wood preserving agents like PCP and diesel range petroleum for the treatment of lumber from the local shoreline mill. Some residues of wood treatment were identified in the Solid Waste Area.

1. OBJECTIVE

An environmental forensic investigation was conducted at the Ashland Lakefront Superfund Site (Site) as part of a Remedial Investigation/Feasibility Study (RI/FS). The objective of this study was to compare the hydrocarbon composition of tar residues collected in subsurface soils from Kreher Park to sediment samples from Site and Reference Areas. Specifically, this investigation was designed to evaluate the compositional diversity and likelihood of multiple tar origins in the study area.

2. SITE HISTORY

The Ashland NSP Lakefront Superfund Site (the "Site") consists of land and sediment located along the shore of Lake Superior, in Ashland, Wisconsin. The Site contains (i) property owned by Northern States Power Company, a Wisconsin corporation (d.b.a. Xcel Energy, a subsidiary of Xcel Energy, Inc. ("NSPW")), (ii) a portion of Kreher Park, a City owned property fronting on the bay, (iii) the former City Waste Water Treatment Plant (WWTP), also located at Kreher Park, and (iv) an inlet area containing contaminated sediment directly offshore from the former WWTP. The NSPW property, located on an upland area above a bluff face fronting on Kreher Park, is the site of a former manufactured gas plant (MGP) that operated between 1885 and 1947. Kreher Park includes reclaimed lands from the bay filled during the late 1800s and early 1900s when the area was the site of major lumbering operations. The most significant of these operations was the John Schroeder Lumber Company, which operated a variety of wood processing and shipping facilities on the lakefront between 1901 and 1939.

The primary contaminants at the Site are derived from tar. These include volatile organic compounds (VOCs) and a subgroup of the larger list of semi-volatile organic compounds (SVOCs) referred to as polycyclic aromatic hydrocarbons (PAHs). The most abundant compounds from each of these groups include benzene (VOCs) and naphthalene (PAHs). Soils and groundwater at the Site are contaminated with these compounds, as are the offshore sediments in the affected inlet. Additionally, tar is present as a nonaqueous phase liquid (NAPL) in the upper reaches of the ravine on the NSPW property, at isolated areas at Kreher Park including the former "seep" area south of the former WWTP, and in the upper elevations of the deep Copper Falls aquifer. The free-product in the deep aquifer has resulted in a dissolved phase contaminant plume that extends north from the area of the free-product in the direction of groundwater flow, toward the bay. However, a thick clay aquitard (the Miller Creek formation) provides a hydraulic barrier that separates the deep aquifer from the shallow groundwater at Kreher Park and the lake waters in the area of the affected inlet. This separation is demonstrated by the strong artesian pressures measured at Kreher Park that are screened in the Copper Falls aquifer. Free-product is also present in some sediments in the affected inlet.

The Wisconsin Department of Natural Resources (WDNR) has been investigating the Site since contamination was first reported at Kreher Park in 1989. NSPW began investigating its property at the upland/bluff area in 1995. NSPW implemented interim removal actions to mitigate exposure risks to contaminants and to recover free-product coal tar from the deep aquifer. A low-flow pumping system currently extracts free-product from the deep aquifer, treating the entrained groundwater before discharging it to the City of Ashland's sanitary sewer. Additionally, NSPW installed an extraction well at the base of a former filled ravine that was the source of the seep discharge at Kreher Park. This extraction well was part of a larger interim action that included excavation of contaminated materials at the former seep area and placement of a low-permeability cap to eliminate the intermittent seep discharge and mitigate environmental exposure of the associated contaminants.

3. TECHNICAL APPROACH

URS collected soil and sediment samples as part of an RI/FS for the Site. A subset of these samples was submitted for environmental forensic chemistry testing. Reference Area samples were collected on 1) the far side of Chequamegon Bay near Washburn, Wisconsin; 2) a regional shore of Lake Superior near Bayfield, Wisconsin; and 3) near the area where Fish Creek discharges into Chequamegon Bay (Figure 1). Site surface sediment samples (0" to 6") were collected directly off shore from the Kreher Park shoreline (Figure 2). Finally, subsurface soil samples were collected from test pits excavated near 1) the Uncontrolled Solid Waste Disposal Area, 2) the former Coal Tar Dump, and 3) the former Wastewater Treatment Plant (Figure 3). Other samples were collected in 2005 from monitoring wells and pipes buried below Kreher Park (Figure 3). Data from a previous forensic investigation of pipes in a former ravine above Kreher Park were also added to the analysis (Battelle 2002).

NewFields received thirteen subsurface soil samples from test pits, ten monitoring well samples containing NAPL, and fifteen sediment samples (Table 1). These thirty-eight samples were prepared and analyzed by forensic methods as described below.

4. ANALYTICAL METHODS

The samples were prepared and analyzed in accordance with published forensic chemistry methods (Emsbo-Mattingly *et al.*, 2003; Stout *et al.*, 2003; Stout *et al.*, 2002). The samples were analyzed by several methods to provide a detailed description of the observed hydrocarbons covering a broad molecular weight range. Bulk parameters, like TOC and soot analysis, provide a rough context for understanding the sample matrix and distributions of large molecular weight organics. In addition, the high resolution gas chromatography hydrocarbon fingerprints depicted the dominant types of extractable hydrocarbons in the samples, while the mass spectrophotometric methods provided more detailed chemical profiles of PAH compounds in samples potentially impacted by tar, petroleum products, and various anthropogenic background materials. Supplementary measurements of phenols and pentachlorophenol by GC/MS/SIM and organic petrology provide additional lines of evidence for understanding the history of PAH-containing media. We used these data collectively to characterize the types of hydrocarbon materials in the study samples.

4.1 Sample Collection and Shipping

The field team collected samples in June, September, and November of 2005 (Table 1). Sample collection methods and field equipment are described under separate cover (URS 2005).

The field samples were shipped via overnight courier and received between 2°C and 6°C at the Alpha - Woods Hole Lab (AWHL) in Raynham, Massachusetts. Other information related to chain of custody and sample receipt was provided at the end of the attached laboratory reports (Attachments F and G).

The sample ID's used in this report were abbreviated when necessary to simplify the tables and figures used for data presentation (Table 1).

4.2 Total Organic Carbon

Total organic carbon (TOC) was measured according to EPA Method 9060. This method entailed homogenization and acid addition to remove inorganic carbon (e.g., carbonates). Water was removed by heating in an oven at approximately 105°C for at least 4 hours. The pretreated samples were combusted at high temperature (900°C) in a stream of oxygen. Carbon was converted to CO₂ and sulfur and nitrogen containing gases were removed prior to coulombic detection.

4.3 Soot

Soot was measured according to EPA Method 9060 modified. This method used the same pretreated sample described in the TOC method (i.e., carbonates and water were removed from the sample). Labile

carbon (e.g., biogenic or detrital organics) was removed by heating in an oven at 375°C for 24 hours. The conditioned samples were combusted at high temperature (900°C) in a stream of oxygen. Carbon was converted to CO₂ and sulfur and nitrogen containing gases were removed prior to coulombic detection.

4.4 Organic Petrographic Analysis

Organic petrographic analysis was used to determine the relative abundances of selected particle types. Samples were prepared using well published organic petrology methods (Stach et al. 1982). Dried samples were crushed and embedded in a monomeric synthetic resin pellet that was ground and polished. The samples were examined using a Leitz reflected light microscope to identify and measure the frequency of particle types described in Table 4. Samples containing coal were analyzed for vitrinite reflectance to refine the coal classification.

4.5 Sample Preparation for Semivolatile Analyses

Of these thirty-eight samples, fourteen samples contained low solids content (< 50%) that could not be increased by centrifugation. These fourteen samples were air dried in a clean hood for approximately 48 to 96 hours. The solids content of twelve samples improved such that the percent solids approached or exceeded 50%. A second aliquot of these samples were prepared and analyzed (see Table 5 samples Client ID's ending with the "AD" suffix). The solids content of two samples (NS-SOTP106-6 and NS-SOTP111-6) did not rise above 30% (Table 5); therefore, the re-extraction of these samples was not necessary. A detailed inspection of these two samples identified the presence of abundant water saturated wood debris; therefore, the extreme conditions required to dry these samples would have compromised the integrity of the native analyte concentrations and compositions.

The samples collected from groundwater monitoring wells contained NAPL. The high concentration of tar constituents in these samples prevented low level QC spiking and sample preparation procedures. Consequently, the NAPL portion of these samples was diluted in solvent and concentrations were reported on an oil weight basis.

An aliquot of each soil and sediment sample (approximately 30 g wet weight) was fortified with surrogates, dried with sodium sulfate and serially shake extracted with dichloromethane (DCM). The sample extracts were concentrated by Kuderna-Danish and nitrogen blow down techniques. An aliquot of the extract was removed for the analysis of phenols and pentachlorophenol. Sulfur and polar interferences were removed from the remaining extract with a copper powder and alumina, respectively. The sample extracts and diluents were split prior to analysis. The extracts were fortified with internal standards and submitted for GC/FID and GC/MS/SIM analyses (described below).

4.6 High Resolution Hydrocarbon Fingerprint and TPH

The sample extracts were analyzed using a high-resolution gas chromatograph equipped with a flame ionization detector (GC/FID). High resolution GC/FID fingerprints were generated over a broad carbon range (approximately n-C₉ to n-C₄₀) that provided an overall assessment of the semi-volatile hydrocarbons present in each sample. These fingerprints provided information on the dominant extractable hydrocarbons that potentially included pyrogenic PAHs, petroleum products, and detrital vegetation. The measured concentration of hydrocarbons in these samples was reported as Total Extractable Material (TEM). The GC/FID fingerprints for each field and QC sample may be found in Attachment C.

4.7 Polycyclic Aromatic Hydrocarbons (PAH)

The sample extracts were analyzed using a high-resolution gas chromatograph equipped with a mass spectrometer operated in the selected ion monitoring mode (GC/MS/SIM). The instrument was calibrated to allow for quantification of a broad range of 2- through 6-ring PAHs, selected alkylated PAH homologues, selected sulfur-containing compounds (dibenzothiophenes), and other compounds useful for the identification of hydrocarbon sources in the environment. Table 2 presents an inventory of the target

compounds along with abbreviations used in selected figures of this report. The term, EPAPAHs, was used in the discussion in reference to the sum of the 16 individual EPA Priority Pollutant PAH compounds (Table 2). Similarly, the acronym TPAH refers to the sum of approximately fifty PAHs used for the forensic analysis of PAH patterns. Collectively, the concentrations of these target compounds helped qualitatively and quantitatively compare the Study Area samples. The concentrations of PAHs in soil and sediment samples were reported in dry weight units. As part of the discussion, PAH histograms were constructed to summarize the most significant compositional features of the respective PAH fingerprints.

4.8 Saturated Hydrocarbon Fingerprints and Triterpane Biomarkers

The presence and/or pattern of biomarker compounds identified information about the specific source(s) of petroleum or coal residues in the environment (Stout *et al.*, 2002; Peters and Moldowan, 1993). An aliquot of the GC extract was injected into a GC/MS/SIM instrument. Saturated hydrocarbon fingerprints were generated from this analysis (Attachment D). Saturated hydrocarbons are compounds with single carbon-hydrogen bonds in various linear, branched, and cyclic configurations. These fingerprints helped identify the types of petroleum or coal-derived products in the sample. In addition, the laboratory generated triterpane fingerprints (Attachment E). The relative abundances of biomarkers, like hopane, can help identify different types of fossil fuel found in samples.

4.9 Phenols and Pentachlorophenol

The presence and/or pattern of phenols and pentachlorophenol provide evidence of wood treating activities (Emsbo-Mattingly *et al.*, 2001). An aliquot of the sample extract (prior to solid phase cleanup) was injected into a GC/MS/SIM instrument calibrated for phenols and pentachlorophenol (Table 3).

4.10 Visual Presentation of Data

This investigation generated a substantial quantity of chemistry data, both chromatographic and numerical. To present this data in a meaningful manner, we use a variety of visual and graphical techniques to display and explain the most significant features. Largely, we relied upon five methods of data analysis in this report. These include:

- Scatter plots that represent the concentration change in two analytical parameters.
- Gas chromatograms, which present the raw output from analytical instruments used to characterize the hydrocarbon distributions.
- Histograms for graphically comparing detailed PAH composition profiles.
- Data tables, like diagnostic PAH ratios, for comparing source signatures among samples.
- Principal Components Analysis (PCA) loadings and scores plots that simplify the PAH source signatures and compositional comparison among samples.

Whenever possible, color coding and symbols were used to illustrate the most relevant compositional features.

5. RESULTS AND DISCUSSION

We divided the results and discussion into method-specific sections for ease of presentation. This section opens with an overview of the bulk analyte concentrations followed by a discussion of the major hydrocarbon patterns evident in the GC/FID data. Thereafter, we present a more detailed description of the hydrocarbon materials evident in the GC/MS/SIM data. These data helped equate source identification features in the absence of chemical interferences. The PAH data proved most useful for characterizing the soot and tar residues while the saturated hydrocarbon and biomarker fingerprints helped identify the source signatures of materials derived from petroleum or coal.

5.1 General Physical Features

The organic petrology data provided a general framework for understanding the composition of each sample (Table 4). High level tar contamination was observed in the Coal Tar Dump and Pipe samples. Natural mineral matter comprised the dominant fraction of the Solid Waste Disposal Area, Wastewater Treatment Plant, and sediment samples. The highest percentages of coal (solid fossil fuel), coke (devolatilized coal), and slag (an anthropogenic mineral formation created at high temperature) were observed in the Pipe samples. Lower amounts of these materials were observed around the Wastewater Treatment Plant and Coal Tar Dump. Generally, less than 2 percent of the samples were coal or coke in samples from the Solid Waste Disposal Area and sediment locations. When grouped by study area, the general distributions for slag were similar to coke and coal; however, the individual samples with high levels of coal and coke usually contained lower levels of slag. Given the various land uses in the area (MGP, historical wood processing, sewage plant settling tanks, coal dock, road bedding, residential coal burners, railroads, and others), the common occurrence of these materials in all areas was predictable.

An important finding included the distribution of tar impregnated wood (Figure 4). Samples with tar impregnated wood (greater than 1%) were found in the former Coal Tar Dump and buried Pipe samples. When observed in the Solid Waste Disposal and Wastewater Treatment Plant areas, the wood contained little to no tar. These findings were consistent with historical reports of wood preservation in the Coal Tar Dump area. Additionally, the Buried Pipes may have drained wood preservative wastes from the former Coal Tar Dump Area.

5.2 General Chemical Features

Hydrocarbons belong to a diverse group of chemicals with many natural and man made (anthropogenic) sources. This study employed multiple methods designed to measure different classes of hydrocarbons. By comparing trends in these data among samples collected from several study areas, important associations can be made between PAHs and other hydrocarbons. These associations help establish multiple lines of evidence that serve as a basis for identifying the origins of one or more hydrocarbon classes; e.g., PAHs.

The total concentration of EPAPAHs served as a general measure of pyrogenic PAHs (Table 2). The concentration of total EPAPAHs helped evaluate changes in PAH concentrations attributed to tar and combustion residues in comparison with other general parameters measured in this study. By contrast, TOC was an analytical parameter that included several classes of non volatile hydrocarbons (petroleum fuels, tar, soot, and biogenic materials from plants, animals, and detritus). A comparison of Total EPAPAHs to TOC exhibited a weak relationship; large increases in EPAPAH concentrations corresponded to only slight, if any, increases in TOC concentration relative to the Reference Stations (Figure 5a). The lack of a general relationship between TOC and EPAPAHs may reflect varying amounts of wood (high TOC and low PAH) and biogenic substances (high TOC and low PAH) mixed with tar (proportional levels of TOC and PAHs). The concentration of PAHs and TOC appeared to weakly increase in the Wastewater Treatment Plant and Solid Waste Areas. In these areas, tar derived PAHs comprised less than 1% of the TOC. The most clear association between TOC and PAH occurred in the Coal Tar Dump Area where tar was clearly the dominant source of carbon (notice that the concentration of EPAPAHs was approximately 10 to 70% of the TOC concentration).

The concentrations of EPAPAHs and soot identified at least two sample populations (Figure 5b). Samples from the Reference Area locations exhibited a high ratio of soot relative to total EPAPAHs that ranged from 6,600 to 79,000. This positive association in the Reference Areas was attributed to background sources of PAHs; e.g., vehicular and fossil fuel emissions. Site sediment samples approaching this range included SQT02 to SQT06 with ratios of soot:total EPAPAHs ranging from 1,700 to 5,900. Therefore, soot accumulations in this area could account for a significant portion of PAHs in these Site samples. By contrast, tar contaminated samples from the Coal Tar Dump and Pipe samples contained dramatically lower ratios of soot:total EPAPAHs in the range of 0.6 to 16. The low levels of soot relative to PAHs in these samples were attributed to large molecular weight carbon residues (e.g., lampblack, coal, or coke). Low abundances of soot relative to PAHs were also observed at locations

TP107, TP111, SQT01, and SQT07; therefore, it is possible that tar was a significant source of soot at these locations.

The concentration of EPAPAHs and Total Extractable Material (TEM) demonstrated that abundances of PAHs, fossil fuels, combustion byproducts, and plant materials (all constituents of TEM) in most Site sediment locations were consistent with regional background (see dashed boundary in Figure 5c). These hydrocarbon concentrations were consistent with urban sediments around the coastal cities across the United States (TEM ranged from 8 to 2350 mg/kg and Total EPAPAHs ranged from 0.008 to 51 mg/kg; Stout *et al.*, 2004). The sample from SQT01 contained slightly higher levels of PAHs than background indicating the likely presence of tar. Sample TP110 contained slightly higher levels of TEM and comparable levels of PAHs relative to the Reference Area samples and likely indicated slightly higher levels of hydrocarbons derived from plants or petroleum. The remaining samples contained EPAPAHs greater than 100 mg/kg and were clearly distinct from background. Many of the samples from the Solid Waste Area plus GW110 contained higher levels of TEM relative to EPAPAHs indicating the presence of higher levels of petroleum. By contrast, samples from the Coal Tar Dump generally contained higher levels of EPAPAHs relative to TEM suggesting the dominant presence of tar.

The relationship of EPAPAHs and Total PAHs (TPAHs) further refined the evaluation of combustion and tar derived PAHs (Figure 5d). In this plot, EPAPAHs represented tar and combustion materials while TPAHs represented tar, combustion, and petroleum derived PAHs. Accordingly, samples that fall along the central diagonal axis occupied by the Coal Tar Dump samples likely contained combustion and tar derived PAHs. PAHs in samples within the boundary or ambient conditions from the Reference Area were primarily derived from combustion while those to the upper right of this boundary contained progressively greater amounts of tar. Samples that plotted to the upper left of the central diagonal axis occupied by the Coal Tar Dump samples contained higher levels of petroleum derived PAHs (e.g., SQT09, SQT03, and GW110). The differences between petroleum and combustion derived PAHs are better illustrated on a molecular level as discussed in subsequent sections.

The concentration of EPAPAHs and Total Phenols helped identify the presence of wood treating preservatives (Figure 5e). Oxygenated aromatic compounds, like phenol and methyl phenols, are present at high levels in coal tar and low levels in carburetted water gas and oil gas tars. These phenols have antibiotic properties and are desirable constituents in wood preservatives. It is acknowledged that under suitable conditions, phenols are also produced naturally; hence, the common observation of Total Phenols less than 1 mg/kg in background locations. The higher levels of Total Phenols generally corresponded with higher levels of EPAPAHs, especially in the Coal Tar Dump, suggesting that wood preservation occurred in this area.

The relationship between EPAPAHs and pentachlorophenol (PCP) provided additional evidence that wood preservation occurred in the Kreher Park Area (Figure 5f). PCP was commonly used for wood preservation (Emsbo-Mattingly *et al.*, 2001; AWWA, 1974). It was frequently detected within the Coal Tar Dump, Solid Waste, and Wastewater Treatment Plant Areas. In addition, selected sediment samples from the Site sediment Areas also contained PCP. Samples from the Reference Areas and numerous samples throughout the study area contained no detectable PCP. Among the samples with detectable levels of PCP, the concentration of EPAPAHs and PCP was proportional suggesting a common origin in the form of tar fortified with PCP. The detection of PCP in all of the Clay Pipe samples also suggested that the pipe may have acted as a conveyance for the wood preservative. Variability in the abundance of EPAPAHs relative to PCP was likely caused by differing rates of degradation throughout the study area.

5.3 Dominant Hydrocarbon Signatures

High resolution hydrocarbon fingerprints (GC/FID) revealed the dominant hydrocarbon patterns in environmental samples. The principal patterns of interest in this study included organic residues of thermal decomposition (e.g., soot, creosote, and tar-based asphalt) and petroleum (e.g., diesel, heavy fuel oil, and petroleum asphalt) material. These patterns were identified by characteristic assemblages of saturated and aromatic hydrocarbons.

Many subsurface soil and NAPL samples within the Kreher Park Area contained tar in various states of weathering. Lightly weathered tars have high levels of naphthalene and other volatile aromatic compounds (Figure 6a). Environmental weathering preferentially removes these more labile substances primarily by evaporation, dissolution, biodegradation, and other processes. Moderately weathered tars are left with lower levels of 2-ring PAHs and abundant 3-ring PAHs (Figure 6b). Heavily weathered patterns exhibit lower levels of 2- and 3-ring PAHs compared to 4-ring PAHs (Figure 6c). These high resolution hydrocarbon fingerprints identified commingling with non-tar derived materials such as diesel and heavy range petroleum (Figure 6c). The variable presence of petroleum among tar contaminated samples indicated that the petroleum and tar were independently released. Mixtures of tar and petroleum were observed towards the middle of the former Coal Tar Dump while samples around the boundary of the Coal Tar Dump contained primarily tar.

Samples from the Solid Waste Area exhibited a range of moderately (Figure 6d) to heavily (Figure 6e) weathered tars. Commingling with diesel and heavy range petroleum was very common in the Solid Waste Area (Figures 6d, 6e, and 6f). In some locations, degraded diesel and heavy range petroleum were the dominant hydrocarbon constituents (Figure 6f).

The highest levels of diesel range petroleum were observed near the Wastewater Treatment Plant (Figure 6g). Other samples in this area contained lower levels of mixed tar and petroleum (Figure 6h). Beginning in 2003, tar appeared in a monitoring well on the northwest corner of the Wastewater Treatment Plant on the shoreline boundary with Chequamegon Bay. Although similar to several Coal Tar Dump samples, this lightly weathered tar (Figure 6n) appeared isolated by compositionally distinct samples collected at intermediate locations along the southern boundary of the Wastewater Treatment Plant (Figure 6g and 6h).

Oily soils were collected from two pipes running along the southeast boundary of Kreher Park. The southwestern most section of pipe was located near the former Solid Waste Area. Samples from this section of pipe contained tar with little weathering (Figures 6i and 6j). Samples from the north eastern section of pipe contained moderately weathered tar mixed with middle distillate petroleum (Figures 6k and 6l). The difference in the degree of tar weathering and the presence of middle distillate in the north eastern section of pipe suggested that the pipes were not connected. The composition of tar in the southwestern pipe was predominantly tar while the field samples collected near the pipe (e.g., TP106, TP107, and TP109) contained varying types of petroleum. Similarly, the mixture of tar and petroleum in the north eastern section of pipe differed from the dominant tar signatures in nearby samples (e.g., GW118 and GWTW09 (Figure 6m)). Therefore, the pipes did not appear to be the primary conduit of contamination in either the Coal Tar Dump or Solid Waste Areas.

Several Site sediment samples contained tar. The highest abundance of tar was observed in SQT01 (Figure 6o). SQT07 and SQT08 contained lesser amounts of tar. The pyrogenic PAH patterns were obscured by hydrocarbons derived from non-tar sources in the high resolution hydrocarbon fingerprints of samples collected further offshore (Figures 6p and 6q). The dominant hydrocarbons in most Site sediment samples bore a close resemblance to the Reference Area sediments around Ashland (Figure 6r) and Washburn (Figure 6s). The variable nature of background hydrocarbons was evident in the higher concentration and complexity of Reference Area sediments near populated areas like Bayfield (Figure 6t) compared to less populated and undeveloped areas like the western corner of Chequamegon Bay (Figure 6u). Many of these unidentified hydrocarbons were attributed to anthropogenic sewage and detrital material.

5.4 PAH Patterns

The concentration and distribution of polycyclic aromatic hydrocarbons (PAHs) provided greater detail and specificity about the type of petroleum, tar, plant material, or anthropogenic background materials in the field samples. For example, petroleum possesses a petrogenic PAH pattern consisting of low parent abundance relative to the alkylated PAHs; e.g., $C_0 < C_1 < C_2$, where C is the compound and # is the

number of alkyl groups. By contrast, pyrogenic PAHs form during the partial combustion or pyrolysis of organic matter. A pyrogenic PAH pattern exhibits high parent abundance relative to the alkylated PAH; e.g., $C0 > C1 > C2$, before weathering. When ordered from left to right by increasing alkylation within a homologue group, petrogenic PAHs rise and fall with a bell-shaped curve (see petrogenic $N0 < N1 < N2 > N3 > N4$ profile in Figure 7b) or upwards sloping profile (see petrogenic $NBT0 < NBT1 < NBT2 < NBT3$ profile in Figure 7f) while relatively unweathered pyrogenic PAHs slope downwards (see pyrogenic $N0 > N1 > N2 > N3 > N4$ profile in Figure 7a). Finally, diagenetic PAHs, like retene and perylene, form naturally in sediments from the decomposition of vegetation. The presence of these compounds typically indicates the presence of debris from land plants.

Forensic scientists employ diagnostic concentration patterns and compound ratios to help identify the presence of PAHs from various sources and states of weathering. At the outset, it should also be noted that these concentration ratios are more reliable source indicators than the peak heights used in the simpler hydrocarbon fingerprinting due, in part, to the potential presence of interferences (e.g., QC compounds, phthalates, halogenated organics, and others) and subtle chromatographic changes (peak widening) that can occur in the GC/FID fingerprints. Consequently, we used the more reliable PAH data for the definitive characterization of PAH sources.

A simple PAH weathering scheme helped evaluate the degree of pyrogenic PAH weathering (Emsbo-Mattingly et al. 2003). Accordingly, the four stages of weathering are established based on the relative abundances of major PAH constituents, as follows:

- Light Weathering occurs when naphthalene (N0) is greater than phenanthrene (P0),
- Moderate Weathering occurs when P0 is greater than N0 and pyrene (PY0).
- Heavy Weathering occurs when PY0 is greater than P0, chrysene (C0) and benzo(a)pyrene (BAP)
- Severe weathering occurs when C0 or BAP is greater than PY0.

These states of weathering are helpful for understanding the general composition of the tar. For example, lightly weathered tar contains abundant 2-ring PAHs and is generally more mobile in the environment. Moderately weathered tar contains abundant 3-ring PAHs and is generally less mobile. Heavily and severely weathered tars contain abundant 4- to 6-ring PAHs and are often solidified in the absence of commingling hydrocarbons; e.g., petroleum distillate or solvent. Table 6 summarizes the PAH weathering state in the various field samples.

As evident in the high resolution hydrocarbon fingerprinting data discussed previously, many of the Site samples were dominated by pyrogenic PAHs consistent with partially combusted (e.g., soot) or carbonized (e.g., tar materials) organic material. For example, GW118 (Figure 7a) contained a full range of 2- to 6-ring pyrogenic PAHs. This lightly weathered material contained high abundances of 2- and 3-ring PAHs relative to 4- to 6-ring pyrogenic PAHs. In various states of weathering, the more recalcitrant portion of this PAH pattern was commonly observed in tar residues throughout the Coal Tar Dump area.

Many of the NAPL containing samples collected throughout Kreher Park consisted of diesel range petrogenic 2- and 3-ring PAHs mixed with tar derived 3- to 6-ring PAHs (see GW117 in Figure 7b). The heavily weathered nature of many of these tars suggested that they were dissolved with the commingled petroleum. The specific list of tar-NAPL containing samples likely dissolved by petroleum included GW103, GW107, GW110, and GW117. By contrast, GW112 and GW118 (Figure 7a) contained higher levels of lighter aromatic hydrocarbons associated with flowable tars. GW112 also contained fairly high levels of diesel range petroleum that may have enhanced its mobility.

Samples in the Solid Waste Area commonly contained a wide variety of PAH patterns that differed from those observed in the Coal Tar Dump. For example, the tar residue in TP108 (Figure 7c) contained relatively high levels of dibenzothiophenes relative to phenanthrenes (DBT2/PA2 and DBT3/PA3) and very low levels of fluoranthene (FL0) relative to pyrene (PY0) compared to samples from the Coal Tar

Dump (Table 7). This pattern was not observed in other samples in the Kreher Park study area or proximal sediments. The PAH pattern in other areas of the Solid Waste Area differed from Coal Tar Dump samples in the form of slightly enriched levels of anthracene (A0) relative to phenanthrene (P0) (Table 7). This enrichment is commonly observed in refined tar products (Rhodes 1945), like creosote. TP100 (Figure 7d) represents an extreme example of this A0 enrichment. TP100 also exhibited high levels of 5- and 6-ring PAHs relative to 4-ring PAHs. This enrichment of 5- and 6-ring PAHs is commonly observed in coal tar pitch used historically to preserve building materials, like tar paper and perhaps lumber.

The sediment samples contained complex assemblages of PAHs. The most common PAH pattern in the Site sediment and Reference Areas was overwhelmingly dominated retene (a phenanthrene structure with 4 alkylated groups and member of the PA4 homologue group) naturally produced from degraded pine tree debris (Figure 7e). It should be noted that retene can cause a positive interference with the tri alkyl-phenanthrene (i.e., PA3) homologues at high levels (Figure 7e). In addition, the sediment samples contained petrogenic 2- to 4-ring PAHs likely from diesel and heavy range petroleum mixed with pyrogenic 3- to 6-ring PAHs attributed to combustion products (Figure 7f). These background signatures were evident in many Site sediment samples, like SQT06. However, some of the Site sediments closer to the shoreline, like SQT01, exhibited PAH patterns from tar residues in the Coal Tar Dump and Solid Waste Disposal Area.

5.5 Diagnostic PAH Ratios and Principal Components Analysis (PCA)

Many of the compositional features discussed in the preceding section can be represented mathematically in the form of a ratio of the concentrations of two PAH analytes (Table 7). For example, when accurately measured, the ratio of fluoranthene (FLO) to pyrene (PYO) is one of many reliable parameters for relating PAH-containing material in a source area to fugitive residues in an associated release area. Other ratios that differentiate PAH assemblages based on the enrichment of organic sulfur, parent PAH, five-member carbon rings, and anthracene are characteristic of unique PAH origins. In complex mixtures of PAHs, these ratios are collectively useful for differentiating one PAH source from another.

We can view many of these compositional features simultaneously in all of the study area samples with Principal Components Analysis (PCA)¹. This multivariate technique produces scores and loadings that statistically simplify the interpretation of PAH trends among the study area samples. The primary objective of the PCA conducted for this study was to aid in the classification of field samples based on their chemical similarities or differences, without any pre-classification as to their nature/source(s). Prior to PCA, the ratios were z-score normalized to reduce the effect of widely varying ranges among PAH ratios. In this report, the results of a PCA are presented using 2-dimensional factor scores and loadings plots. In the loadings plot, analytes that grouped together possessed a high degree of correlation while widely spaced analytes were uncorrelated or negatively correlated. In the scores plot, the source specific nature of the PAH ratios means that spatial proximity of samples on the scores plot is proportional to the compositional similarity. In short, samples that grouped together were compositionally similar while widely spaced samples were compositionally distinct.

The samples included in this investigation fell into four general categories. First, samples with enriched levels of parent PAHs plotted together towards the upper right of the loadings plot (Figure 8a). Samples containing enriched levels of parent PAHs plotted towards the upper right of the scores plot (Figure 8b). The higher degree of pyrogenicity was observed in the Coal Tar Dump, some Site sediments (e.g., SQT01 and SQT07), and WDNr pipe system samples. The PAHs in these samples likely shared a common origin (e.g., TP113, TP116, and TP118 in Figure 8b). Second, the lower center and lower right

¹ Principal Component Analysis (PCA; Pirouette, Version 3.02, Infometrix, Seattle, WA) is a factor analysis method that generates new independent variables (i.e. factors) that are linear combinations of the original input variables (e.g., chemical concentration ratios). This method reduces the dimensionality of the data to a few important "principal components" (axes) that best describe variations in the data. The first axis (1st PC) demonstrates the most prominent trend and successive axes (2nd PC, 3rd PC, etc.) demonstrate additional trends in decreasing order of statistical importance.

sections of the loading plot corresponded to enriched levels of organic sulfur (DBT2/PA2 and DBT3/PA3 in Figure 8a). Samples with high levels of organic sulfur were collected from the Solid Waste Disposal and Wastewater Treatment Plant areas (e.g., GW110 in Figure 8b). Samples plotting in the lower center of the scores plot (e.g., TP100 in Figure 8b) also corresponded to higher levels of anthracene (A0) in the loadings plot (i.e., A0/P0 in Figure 8a). Enriched anthracene is consistent with some types of creosote wood preservative. A final compositional grouping includes PAHs with one five-membered ring (e.g., dibenzofuran, fluoranthene, benzo(b)fluoranthene, and benzo(k)fluoranthene) that grouped in the upper left corner of the loadings plot (e.g., DF/F0, (BB+BJK)/BAP, and FL0/PY0 in Figure 8a). Samples with enriched levels of these compounds were formed under different conditions than the tar residues in the Coal Tar Dump (e.g., SQT09, SQT10, and SQT13 in Figure 8b). These samples also contained higher levels of benzo(e)pyrene relative to benzo(a)pyrene. We attributed this property to the possible presence of heavy petroleum not otherwise observed in the study area samples. Collectively, these PAH characteristics were associated with samples that plotted towards the upper left of the scores plot. These samples were clearly diagnostic features of PAHs generated as part of the regional background.

These PCA results provided a framework for more comprehensively illustrating the origins of PAHs among the study area samples. For example, TW11, SQT01, SQT07, and SQT08 plotted with many samples from the Coal Tar Dump (Figure 8b); therefore, these samples likely shared a common origin. By contrast, samples plotting in the middle of the scores plot shared compositional features of multiple sources (Figure 8b). For example, SQT02 and SQT06 exhibited recognizable contributions from Reference Area as well as characteristics of samples from Kreher Park. The intermediate location in which most of the Site sediment samples resided on the PCA scores plot suggested that some Site sediments received PAHs from multiple sources of PAHs at Kreher Park.

5.6 Fugitive Petroleum and Plant Waxes

The saturated hydrocarbon fingerprints identified the chemical profiles of fossil fuels (e.g., petroleum and coal) and plant waxes.

Four classes of saturated hydrocarbons were observed in the study area samples. Within Kreher Park, the most common saturated hydrocarbon mixture consisted of diesel range petroleum with lesser amounts of heavy range petroleum (Figure 9a). The low abundances of normal alkanes relative to isoprenoids indicated heavy biodegradation in most of the samples. A few samples in the Coal Tar Dump contained relatively unweathered normal alkanes in the kerosene range (Figure 9b). Some petroleum mixtures contained more heavy range material than diesel range distillate (Figure 9c). However, the groundwater-NAPL samples contained predominantly biodegraded diesel range material (Figure 9d). The sediment samples predominantly contained plant waxes derived from decomposed land plants (Figures 9e and 9f).

The exact origin of kerosene, diesel, and heavy range middle distillates was unclear. The variable abundances of these materials relative to the amount of PAHs in the test pit samples suggested that these fugitive petroleum products were the result of historical activities at the Kreher Park. Kerosene, for example, was widely used as a heating fuel and solvent. Diesel range material is commonly used in heavy vehicles, residential heating units, commercial heating units, MGP gas oil, and others. When found at MGP sites, low levels of middle distillate can be found commingled with the tar due to its incomplete combustion as a manufactured gas feedstock. In this scenario, diesel range hydrocarbons are present at relatively low levels and only observed after careful isolation in the laboratory. In Kreher Park test pits, the diesel range material is frequently present at very high concentrations. This middle distillate petroleum could also have resulted from historical activities at Kreher Park; for example this distillate may have served as a carrier to improve the penetration of PCP or tar during wood preservation activities (Emsbo-Mattingly *et al.*, 2001; AWP, 1974). Finally, high levels of heavy petroleum may indicate the presence of heavy fuel or asphalt paving.

5.7 Genetic Origins of Heavy Hydrocarbons

Triterpane biomarkers reside in the heavy molecular weight fraction of crude oil and coal. The relative abundances of specific biomarkers help identify the geographic region and conditions under which the crude oil and coal were formed (Peters and Moldowan 1993). The molecular signature of preserved organic matter is a function of the initial mixture of biomass and geochemical processes controlling or influencing the formation of fossil fuel. Having survived millennia under heated and pressurized conditions, selected biomarkers (e.g., triterpanes and steranes) resist the degradation processes that occur in coastal sediment and soil environments. These biomarkers can be used to differentiate the origins of heavy hydrocarbons even when most of the more labile compounds degrade.

Triterpane biomarkers were observed in several samples in the Solid Waste (Figure 10a) and Wastewater Treatment Areas (Figure 10b). The presence of these compounds indicated the presence of heavy range petroleum hydrocarbons. The similarity of the triterpane pattern suggested that heavy petroleum in the Solid Waste and Wastewater Treatment Plant Areas may share a common origin. Other samples in the Solid Waste Area exhibited triterpanes with alternate patterns, and by extension, origins (Figure 10c). The heterogeneity of these source patterns established that a variety of heavy residual materials were present in the Solid Waste Area. Examples of heavy petroleum range material include crude oil, heavy residual oil, petroleum asphalt, lubricating oil, and coal. Samples in the Coal Tar Dump did not contain triterpane biomarkers above the method detection limit; consequently, the chemical residues of heavy petroleum or coal were not detected in soils from this area (Figure 10d and 10e).

Triterpane biomarkers were not detected in the sediment samples (Figure 10f). Rather, the sediment samples exhibited unidentified peaks attributed to immature biomarkers which likely reflect the presence of modern organic material (e.g., vegetation) in the early stages of diagenesis.

6. SUMMARY

This report presents a detailed compositional description of samples collected around the Ashland Lakefront Site in Ashland, WI. The objective of this study was intended to help the project team evaluate the types of tar, petroleum, and wood preservatives potentially in samples from the former Coal Tar Dump, Solid Waste, and Wastewater Treatment Plant Areas. In addition, oiled soils from two pipes buried under the southeastern boundary of Kreher Park were added to the study. The hydrocarbon residues in these Kreher Park locations were compared to additional samples collected in Site sediment and Reference Area surface sediments. To address the project objectives, advanced chemical analyses for PAHs, normal alkanes, isoprenoids, triterpane biomarkers, phenols, and pentachlorophenol were determined on samples collected from the study area.

The results of these analyses yielded the following conclusions:

- Most of the tar measured in the Coal Tar Dump was likely derived from a single source based on the PAH composition. This tar was lightly to heavily weathered. It resembled the PAH composition of selected NAPL samples collected in 2001 from pipes located in a former ravine above Kreher Park.
- Two NAPL samples (NSP-GW-TW-09-1105 and NSP-GW-TW-11-1105) collected from monitoring wells near the Coal Tar Dump and Wastewater Treatment Plant, respectively, contained lightly weathered tar similar to that found in the Coal Tar Dump.
- Sample NS-GW117-0605 was collected in the Coal Tar Dump area as a groundwater sample containing NAPL. This sample consisted of high levels of diesel range material not directly associated with MGP residuals. It is likely that this petroleum helped dissolve heavily weathered tar (solid) with which it commingled. Additional samples of heavily weathered tar entrained in diesel range petroleum (groundwater-NAPL) were collected in the Solid Waste and Wastewater Treatment Plant Areas.
- Most of the hydrocarbons in the Solid Waste Area exhibited a range of source signatures. The tar measured in the Solid Waste Area was frequently distinct from the tar in the Coal Tar Dump based on the PAH composition. For example, NS-SOTP108-Pipe, NS-SOTP107-8, NS-SOTP109-2, and NS-SOTP100-5 were inconsistent with the Coal Tar Dump Area. The high degree of variability was also evident in the distribution of diesel and heavy range petroleums based on the saturate and triterpane fingerprints.
- The Wastewater Treatment Plant samples contained pyrogenic PAHs attributable to both the Solid Waste and Coal Tar Dump areas. Petrogenic PAHs from diesel and heavy range petroleums were also observed.
- Samples collected from two pipes buried below the southeast boundary of Kreher Park contained tar. The more northerly section of pipe contained moderately weathered tar mixed with middle petroleum distillate. The more southerly section of pipe contained lightly weathered tar. The chemical differences between the two sections of pipe suggested they were not linked.
- Site sediment PAHs largely fell in the PAH concentration range of Reference Area sediments. The PAH patterns resembled a mixture of Reference Area and Kreher Park inputs. These samples also contained modern organics associated with degraded vegetation.

- Several lines of chemical evidence supported the historical preservation of wood at Kreher Park. First, pentachlorophenol (PCP) was detected in many samples throughout Kreher Park. Second, PCP was often blended with petroleum distillate or tar prior to wood treatment. In samples containing PCP, the concentration of PCP increased proportionately with tar-derived PAHs. Third, wood preservers favored phenolic compounds. In samples containing phenols, the concentration of phenols increased with tar-derived PAHs. Fourth, wood preservers used diesel range petroleum as a carrier for PCP, and possibly tar, to improve penetration into the lumber products. Diesel range petroleum was found frequently at the site. Fifth, creosote residues were found in the Solid Waste Area. Creosote was a common wood preservative. Sixth, tar impregnated wood was found exclusively in the Coal Tar Dump and buried pipe samples. The presence of tar impregnated wood and PCP in the buried pipes indicated that the pipes may have been used as a conveyance of preservative at the wood treatment facility. Collectively, these lines of evidence suggested that wood preservation likely occurred at the former lumber mill at Kreher Park.

In summary, subsurface samples at Kreher Park contained hydrocarbon mixtures derived from tar and petroleum that were released as part of the historical development of the Ashland shoreline. The Solid Waste Area clearly received a wide variety of PAH containing materials. While some of the tar samples resembled tar from the Coal Tar Dump, the origin of PAHs in many samples was unknown. The Coal Tar Dump contained tar that originated at least in part from up gradient sources (pipes). This tar was likely amended with wood preserving agents like PCP, diesel range petroleum, and creosote for the treatment of lumber produced by the local shoreline mill. Some residues of this operation appeared in the Solid Waste Area.

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